Dual-Phase Inorganic Membrane for High Temperature CO_2 Separation

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Motivation

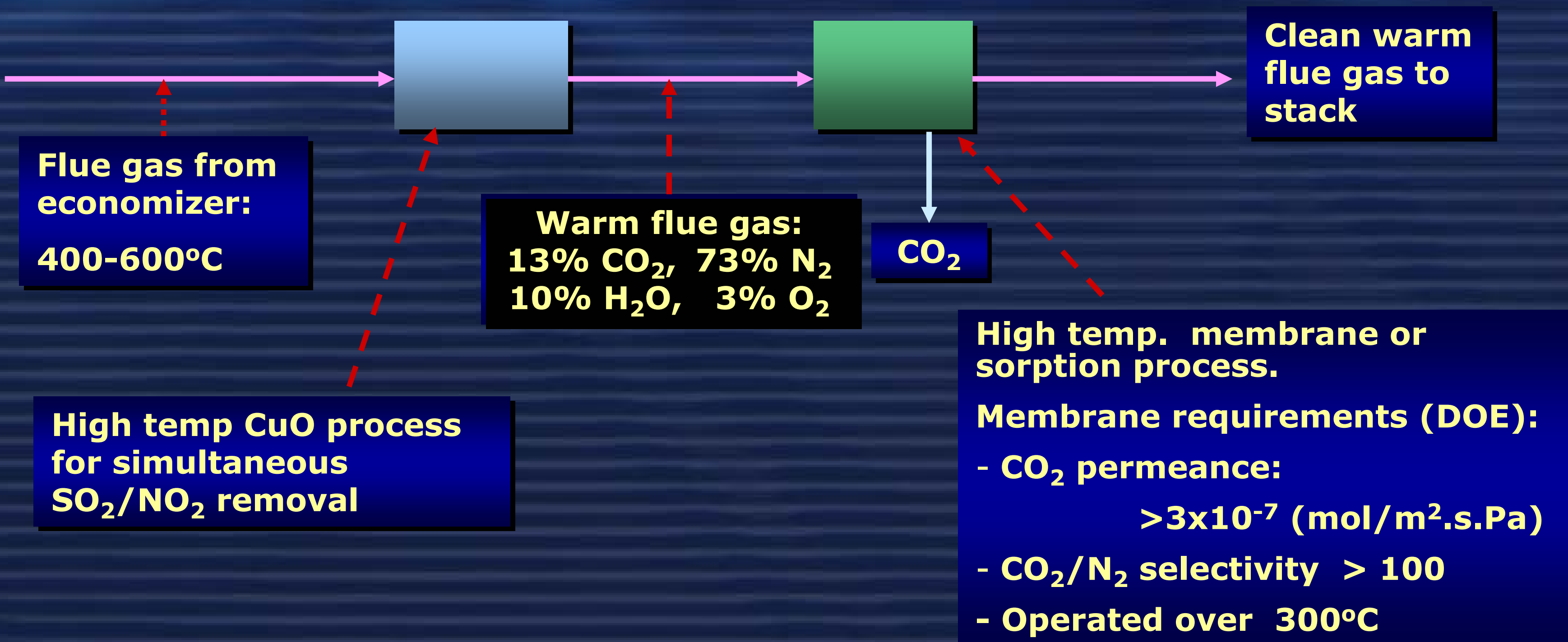
- ***Why do we need to separate CO_2?***

  - Carbon dioxide emits from most industrial facilities
  - Carbon dioxide causes 'Green House effect'
  - Possible use as a feedstock (warm CO_2) to synthesize fuels

- ***Why do we use membrane for CO_2 separation?***

  - Simple, continuous and energy efficient process
  - Applicable to the process at high temperature

Impact of this research

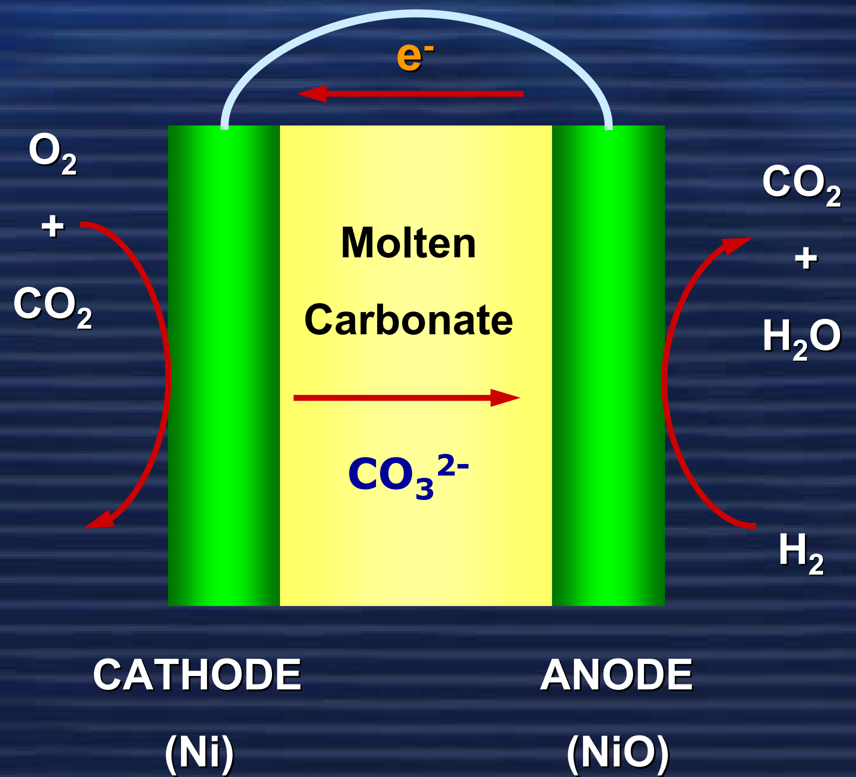


Inorganic membrane for CO_2 separation

- Polymeric membrane (unstable at high temperature)
- Microporous inorganic membrane (low selectivity at T>350^{o}C)
- Ionic conducting membrane (from concept of fuel cell):

  Operated at 400-600^{o}C with high selectivity

Principle of MCFC



Common electrolyte :

Eutectic composition of Li_2CO_3 / K_2CO_3 (62 mol% / 38 mol%)

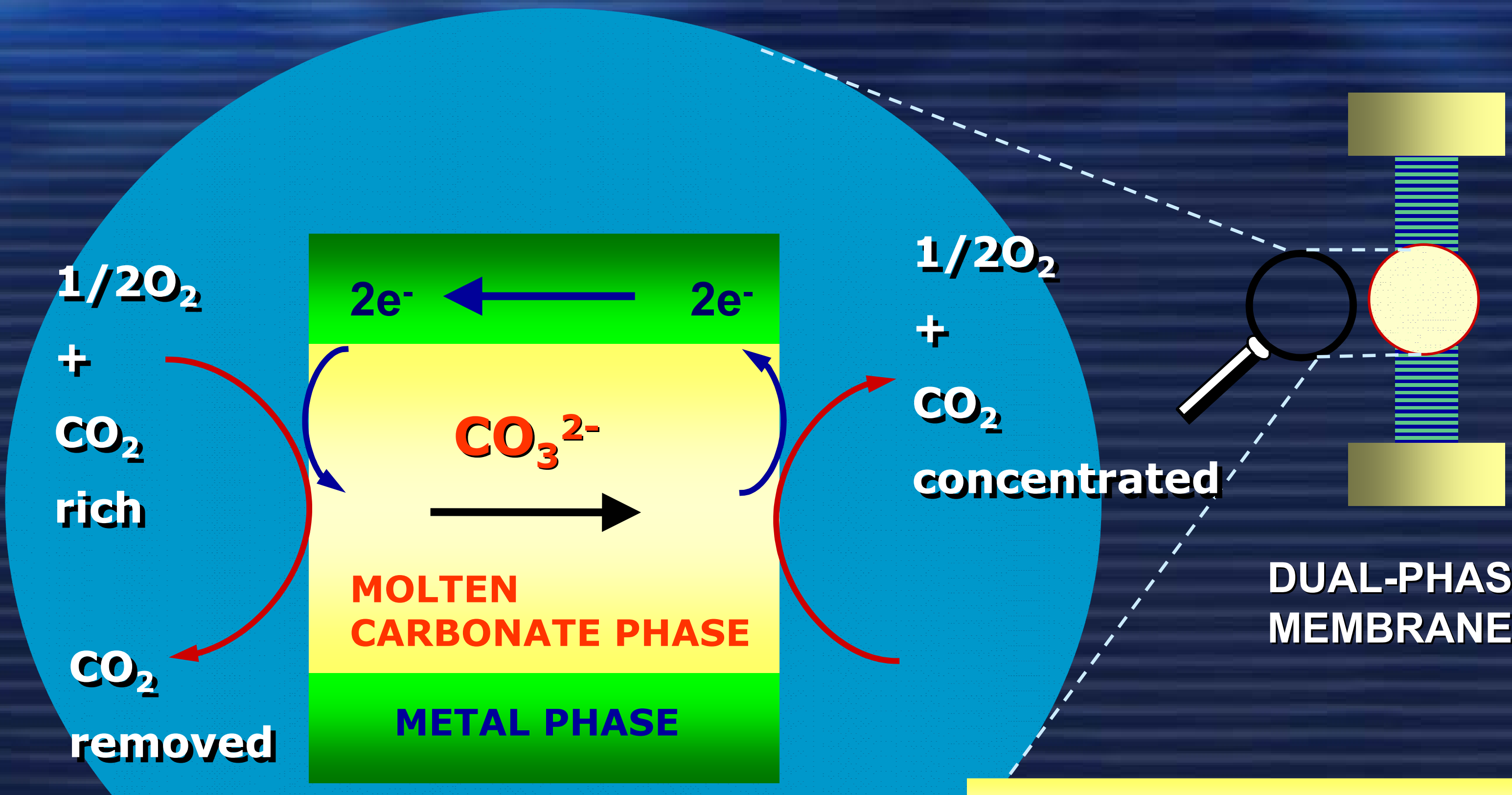
Operating Temperature :

600 ~ 650°C

Major problem :

Precipitation / Contamination of electrodes, reducing performance

Concept of dual-phase membrane



$$CO_3^{2-} \leftrightarrow CO_2 + \frac{1}{2} O_2 + 2e^-$$

Upstream

High P_{co2}

Downstream

Low P_{co2}

Objectives

- **Synthesis of the dual-phase membrane**
  - Prepare dense and stable dual-phase membrane
- **Characterization of dual-phase membrane**
  - Gas-tightness for He and N_2
  - XRD / SEM analysis → Identification of dual phase
- **Design of high temperature seal & cell**
  - Sealing Test with various seals → Gas tight cell design
- **CO_2 separation at high temperature**
  - Permselectivity of CO_2/N_2 (400-600^oC) > 100
  - Permeance of CO_2 (400~600^oC) > 1~5 x10^{-7} mol/m^2.s.Pa

Experimental Strategy

- **Development of methods for membrane preparation (Completed)**

  - Material selection, contact time, temperature, preheating
- **Membrane characterization (Completed)**

  - He gas tightness / XRD / SEM with EDS
- **Designing of high temperature seal and cell (Completed)**

  - He permeation and stability test with various seals
- **Single / Binary gas permeation test (Completed)**

  - gas (He, CO_2, N_2, O_2+CO_2) permeances at various Temp.
- **Separation with multi-component gas (continued)**

  - Multicomponent separation system (CO_2, N_2, O_2 mixture)

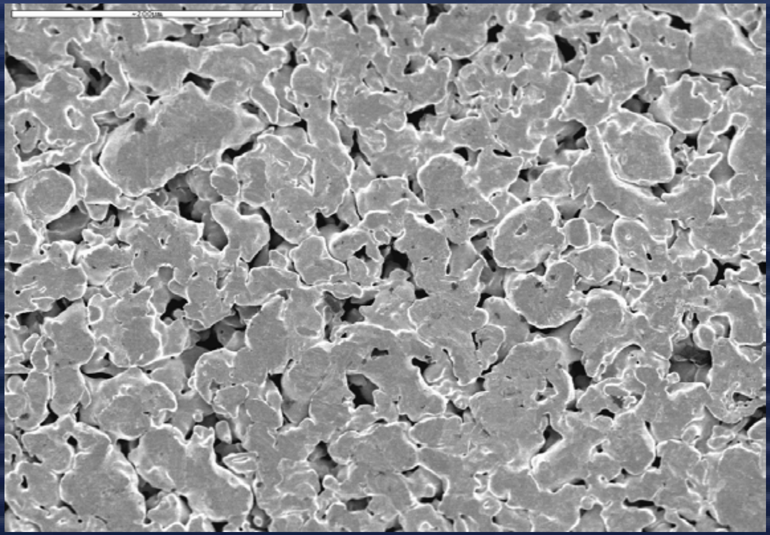
Material Selection

Metal support

General information

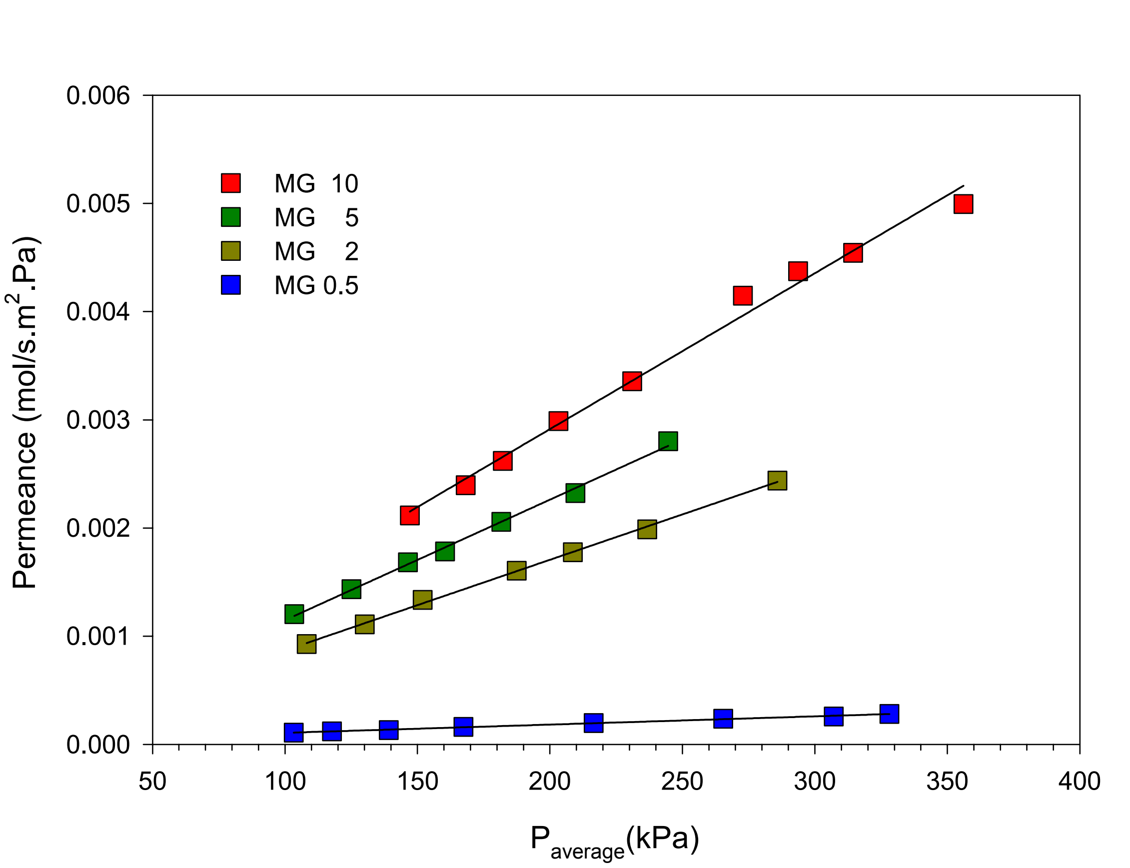
Material	Stainless steel 316
Structure	Spherical particle compacted
Media Grade	0.5, 2, 5, 10
Porosity	25-45%
Pore diameter	1~10μm
Electrical Conductivity	10^4 S/cm

Media Grade 0.5 (SEM, 200x)



- He permeation test → Selection of suitable support

Characterization of metal substrate



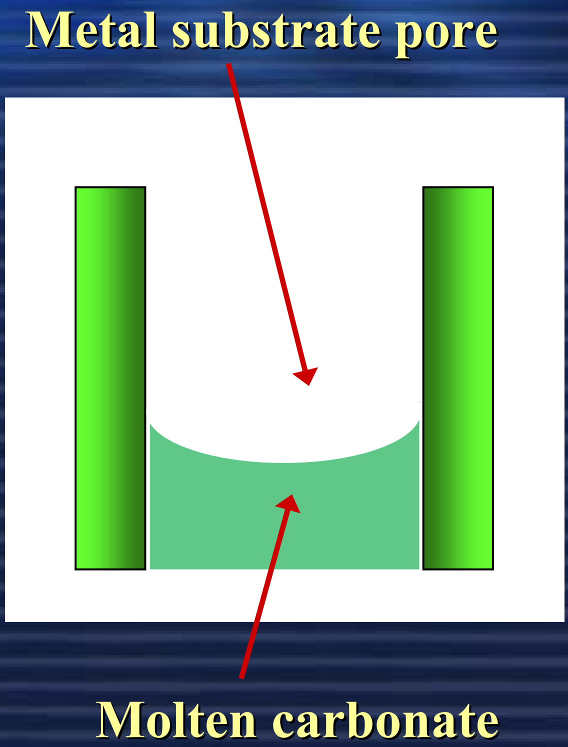
He Permeance vs Average Pressure

Characterization of metal substrate

Parameters related to pore size with various supports

Media grade	b x 10^{-10}	a x 10^{-5}	b/a x 10^{-5}	r_p [μm]	τ	Average pore diameter [μm]
0.5	7.44	3.64	2.05	2.65	3.93	5.30
2	83.84	2.96	28.34	36.75	93.71	73.50
5	111.37	3.45	32.25	41.82	99.22	83.64
10	144.07	3.25	44.34	57.51	152.64	115.02

Molten carbonate infiltration



$$\Delta P = \frac{2\sigma}{R}, r = R\cos\theta$$

$$r = \frac{2\sigma\cos\theta}{\Delta P}$$

where,
σ =237 mN/m^2
Θ=0 for stainless steel

Capillary pressure ΔP=1 atm

↓

Substrate pore size 9μm.

Media grade 0.5 was chosen

Material Selection

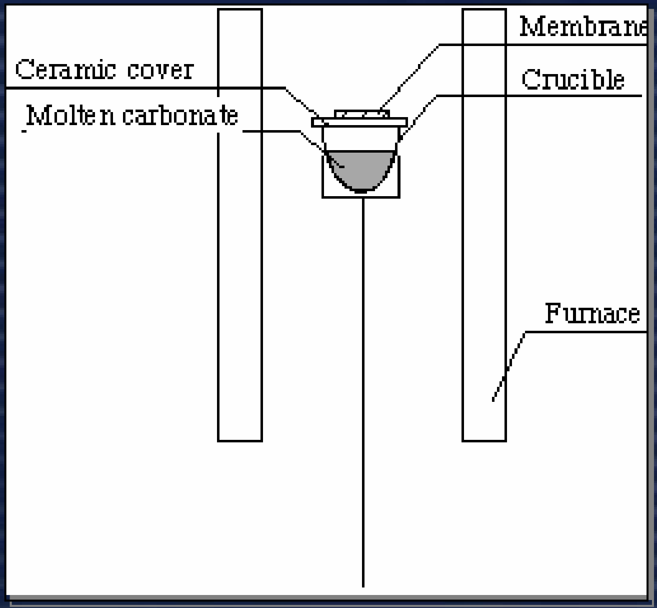
Carbonate Mixture

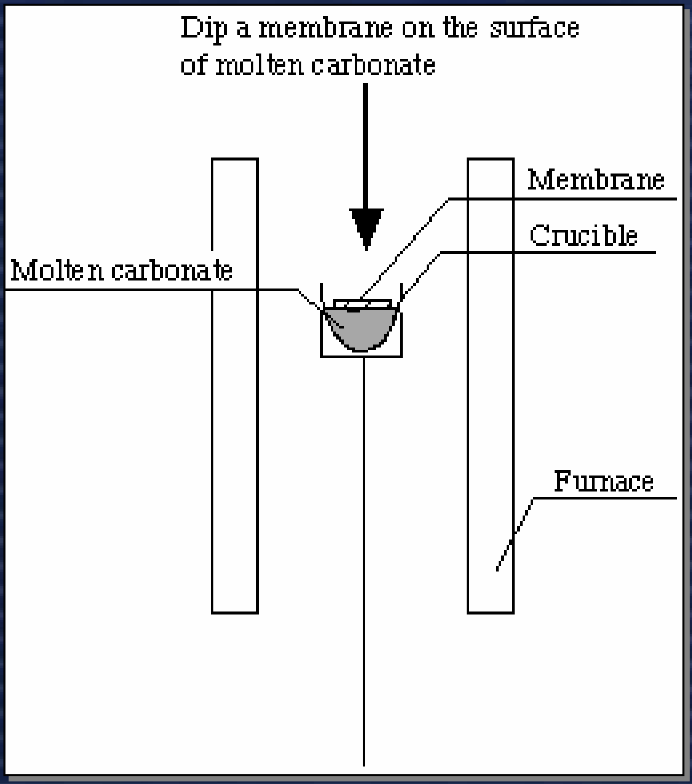
	Li/Na/K Carbonate	Li/K Carbonate	Li/Na Carbonate	Na/K Carbonate
Composition (mol%)	43.5/31.5/25	62/38	52/48	56/44
Melting Point (°C)	397	488	501	710
conductivity (S/cm)	1.24	1.15	1.75	1.17

- Low melting point and high electrical conductivity
  → Li/Na/K (43.5/31.5/25 mol%) was chosen

Preparation of the dual phase membrane

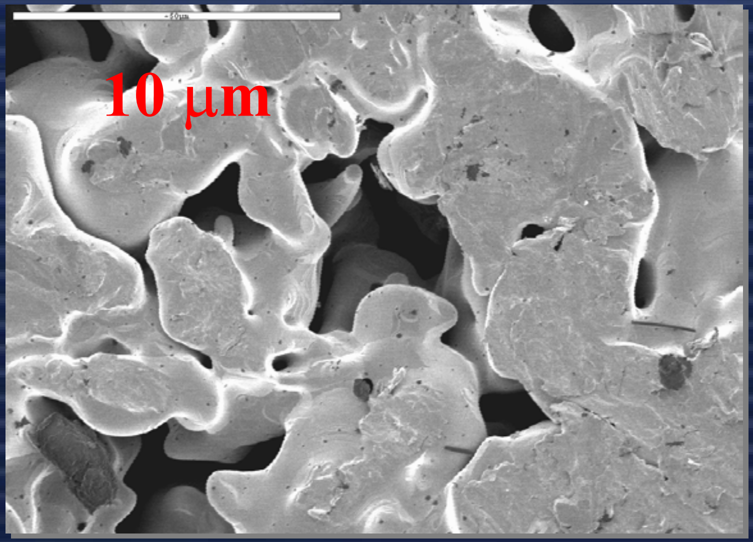
- Mix and melt Li/Na/K carbonate (43.5/31.5/25 mole%)
- Infiltrate molten carbonate into the pores by dipping method.





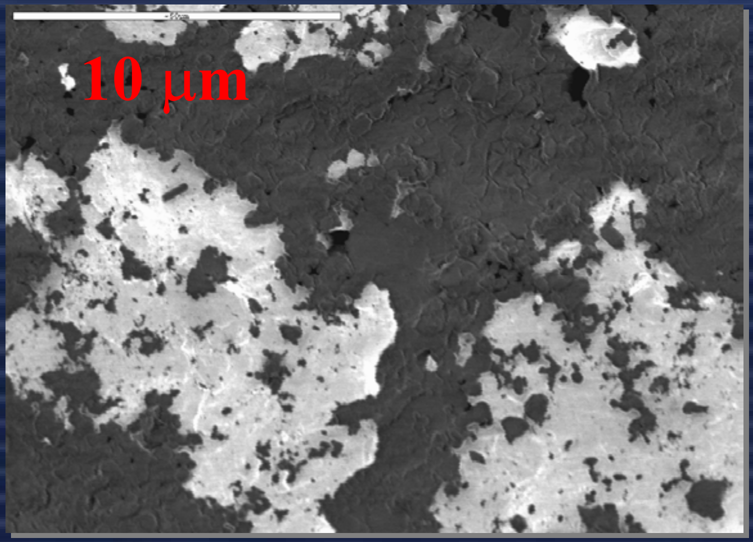
SEM image of dual-phase membrane

- **Before infiltration**



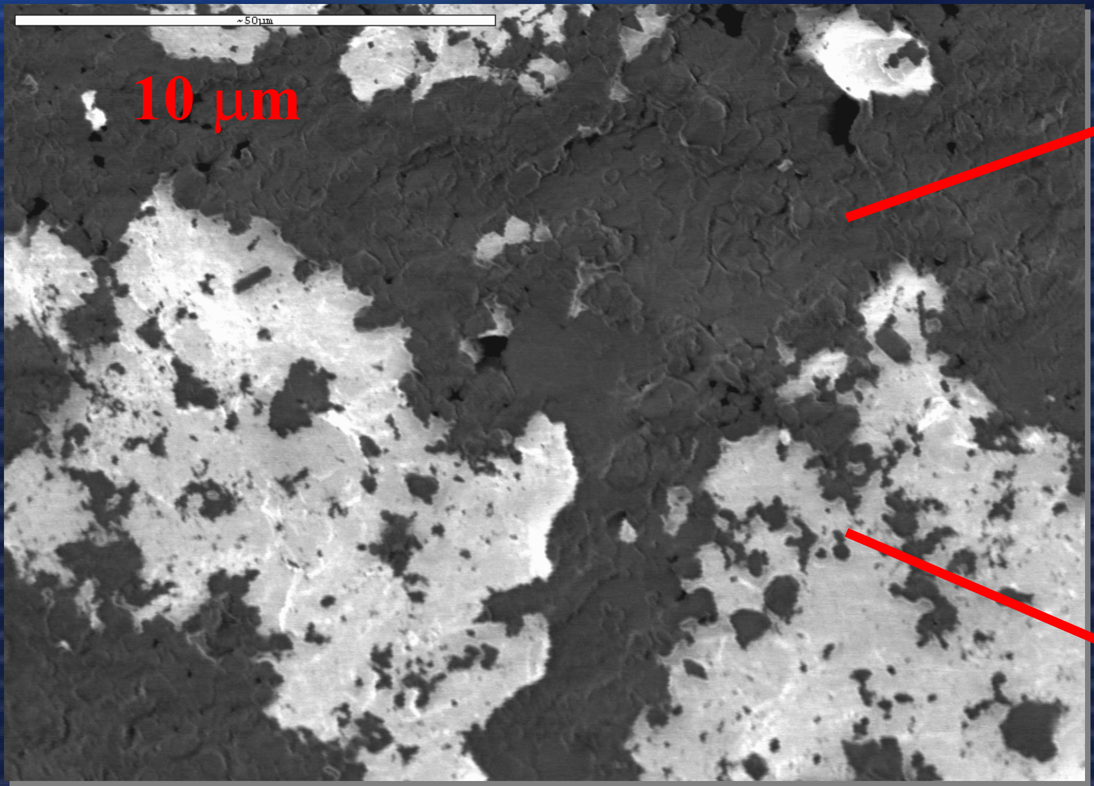
Metal support, 1000x

- **After infiltration**

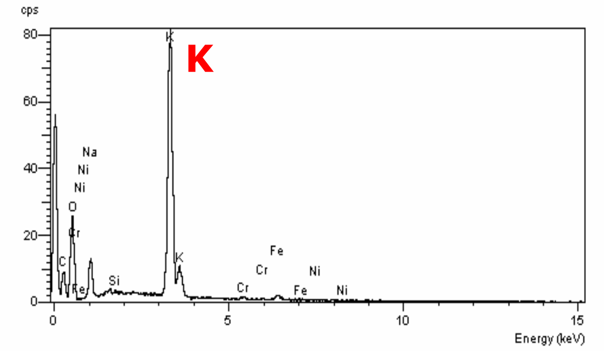


Metal-carbonate, 1000x

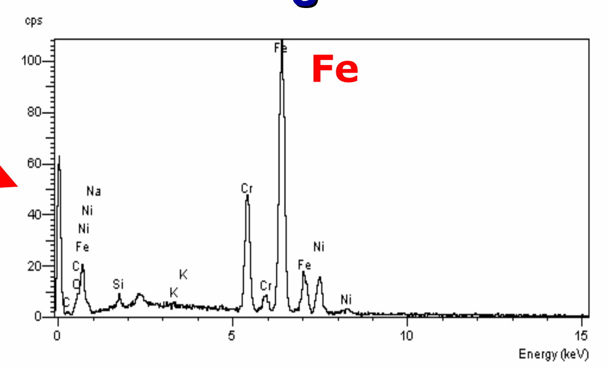
Identification of dual-phase structure



Carbonate rich region

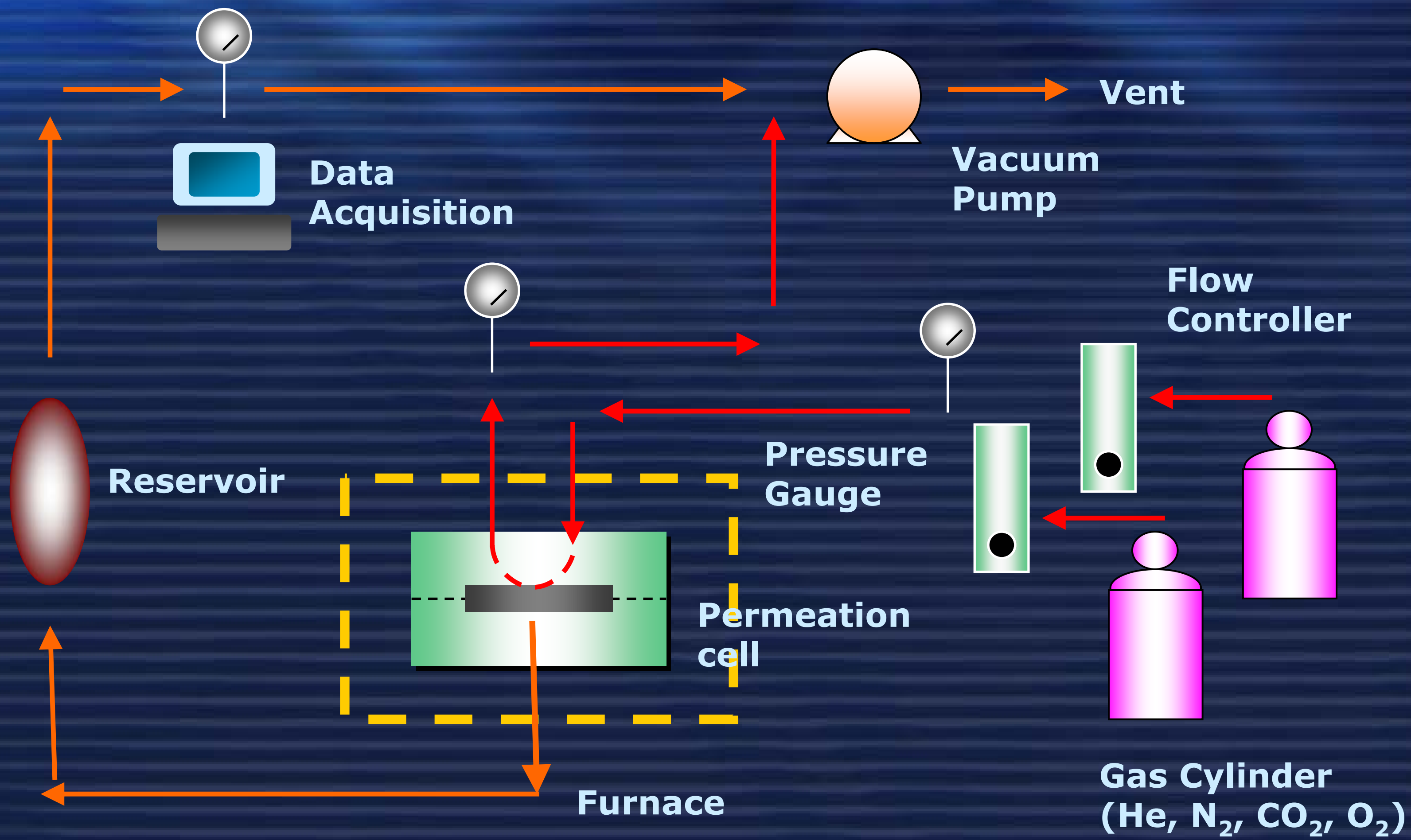


Metal rich region



- Dual-phase membrane is successfully prepared

Experimental Apparatus



unsteady state type Gas permeation setup

Seal design for high temperature

Comparison chart for high temperature seals

Seal	Rubber	Pure Graphite	Graphite Composite	Nickel Alloy	Gold
He Permeance ($mol/s.m^2.Pa$) at R.T.	$2x10^{-10}$	$1x10^{-7}$	$8x10^{-9}$	$7x10^{-9}$	$6x10^{-10}$
He Permeance ($mol/s.m^2.Pa$) at $450^{o}c$	-	$3x10^{-7}$	$3x10^{-9}$	$7x10^{-9}$	$3x10^{-10}$
Stability at high Temp.	Burn	Vaporization	Vaporization	inert	Inert

Theoretical permeation flux

- **Wagner Theory**

$$J(CO_2) = -\frac{RT}{16F^2L}\int_{\ln P_{CO_2}}^{\ln P'_{CO_2}} \frac{\sigma_{el}\sigma_{ion}}{\sigma_{el}+\sigma_{ion}} d\ln P_{CO_2}$$

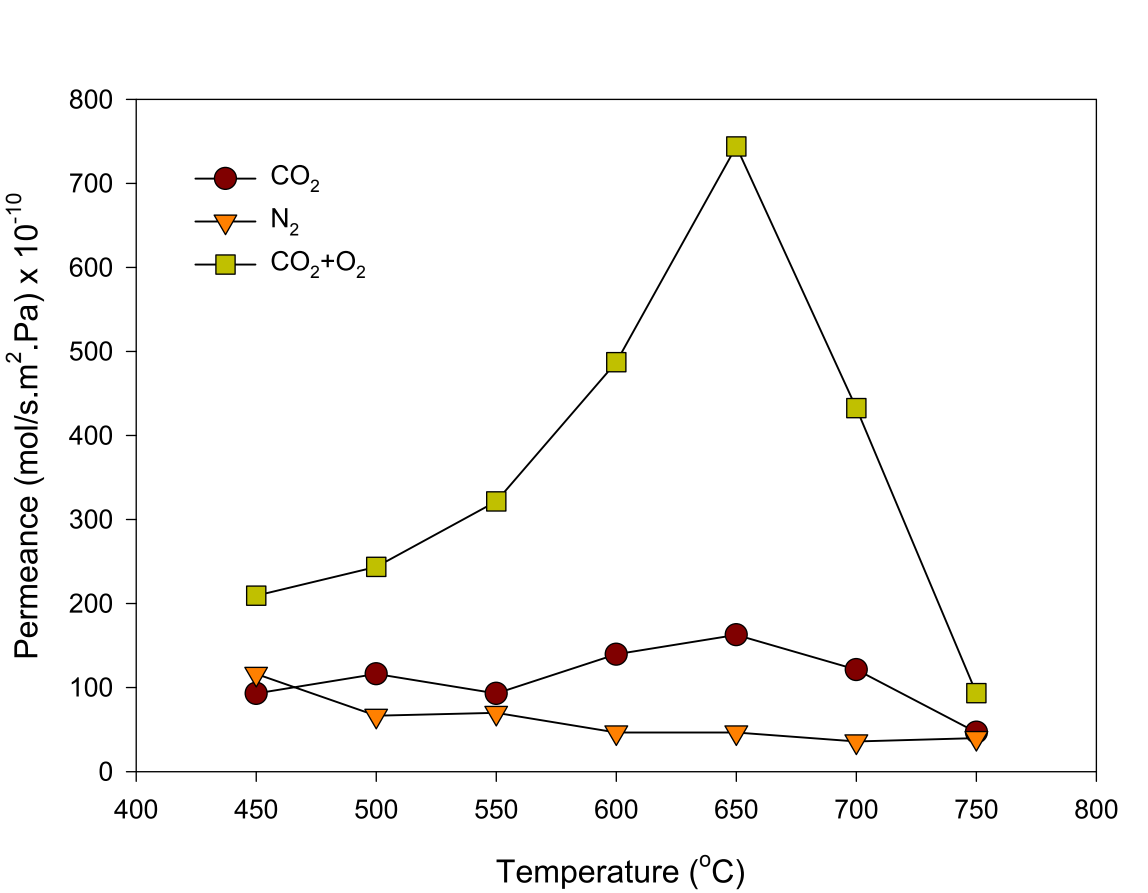
F **(Faraday constant) : 9.65 x 10^4 C/mol ,** ***R*** **(Gas constant),** ***d*** **(Thickness)**

$$J(CO_2) \propto \frac{\sigma_{el}\sigma_{ion}}{\sigma_{el}+\sigma_{ion}} \cong \sigma_{ion} \quad (\because \sigma_{el} >> \sigma_{ion})$$

σ_{ion} **(CO_3^{2-} conductivity) : 0.5-2 S/cm (at 600 °C, Pco_2 = 1/3 atm)**
σ_{el} **(Electronic conductivity : 10^4 S/cm**

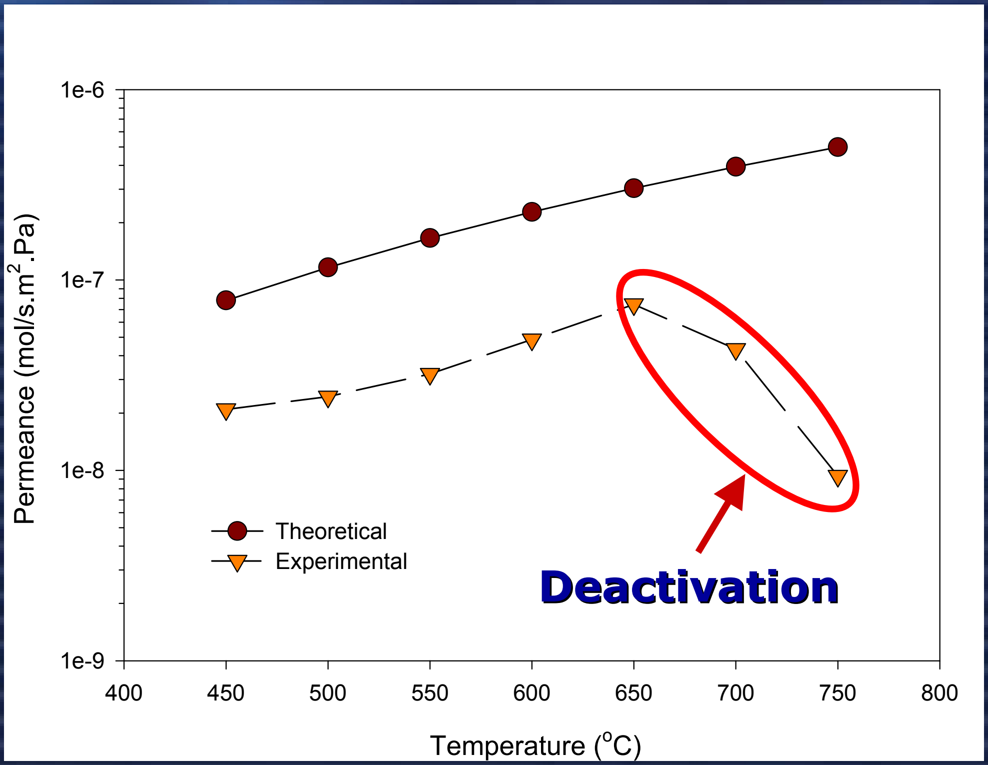
Rate determining variable : σ_{ion}
CO_2 permeance : 2~10 x10^{-7} mol/m^2.s.Pa (for 1 mm thick membrane)

Single / Binary gas permeation test



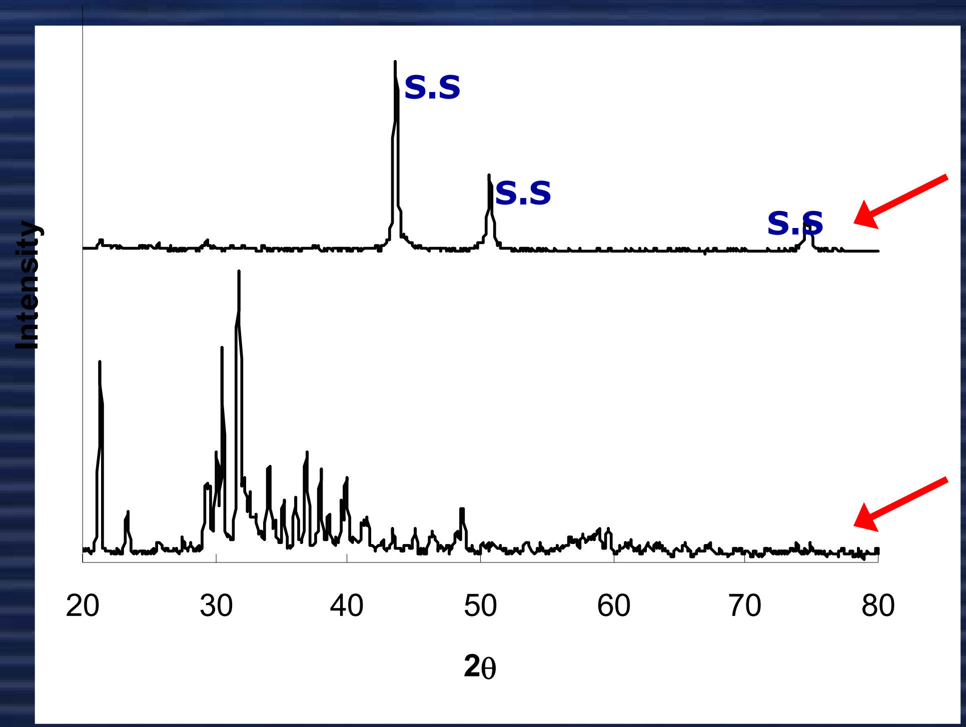
Gas permeation at various temperature (450-750^{o}C)

Comparison of permeation flux



Deactivation occurred at higher than 650^{o}C,

Structure of metal-carbonate membrane

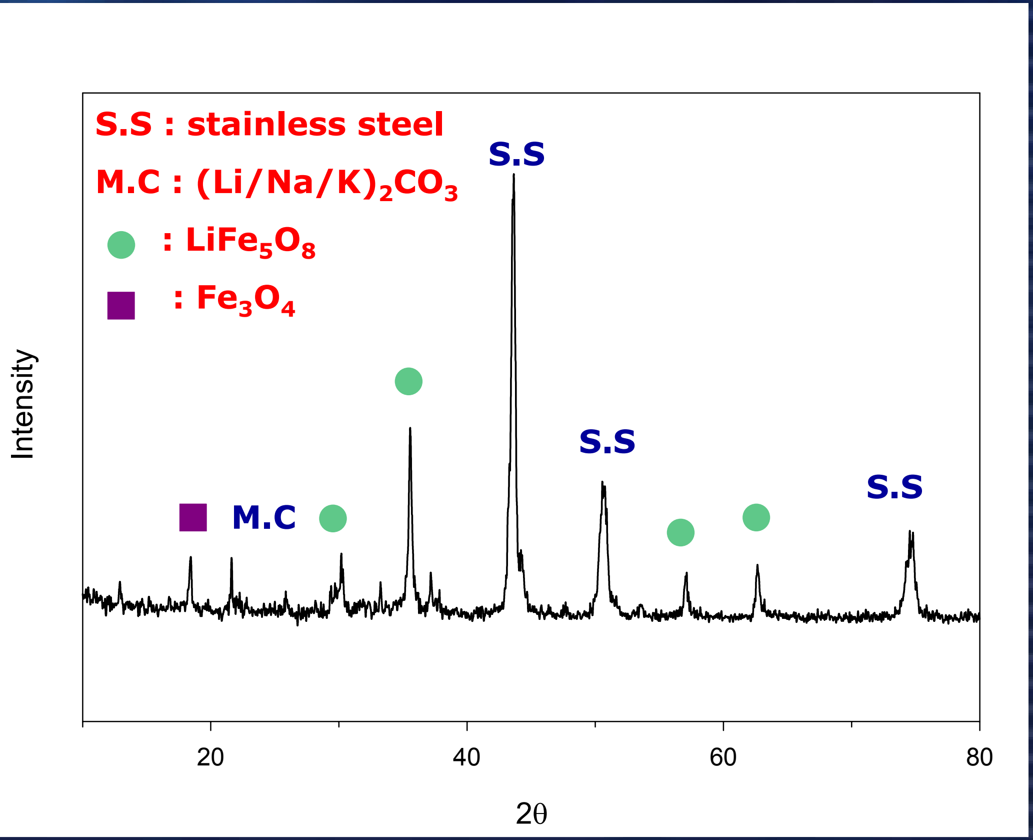


Dual-phase membrane

Li/Na/K carbonate

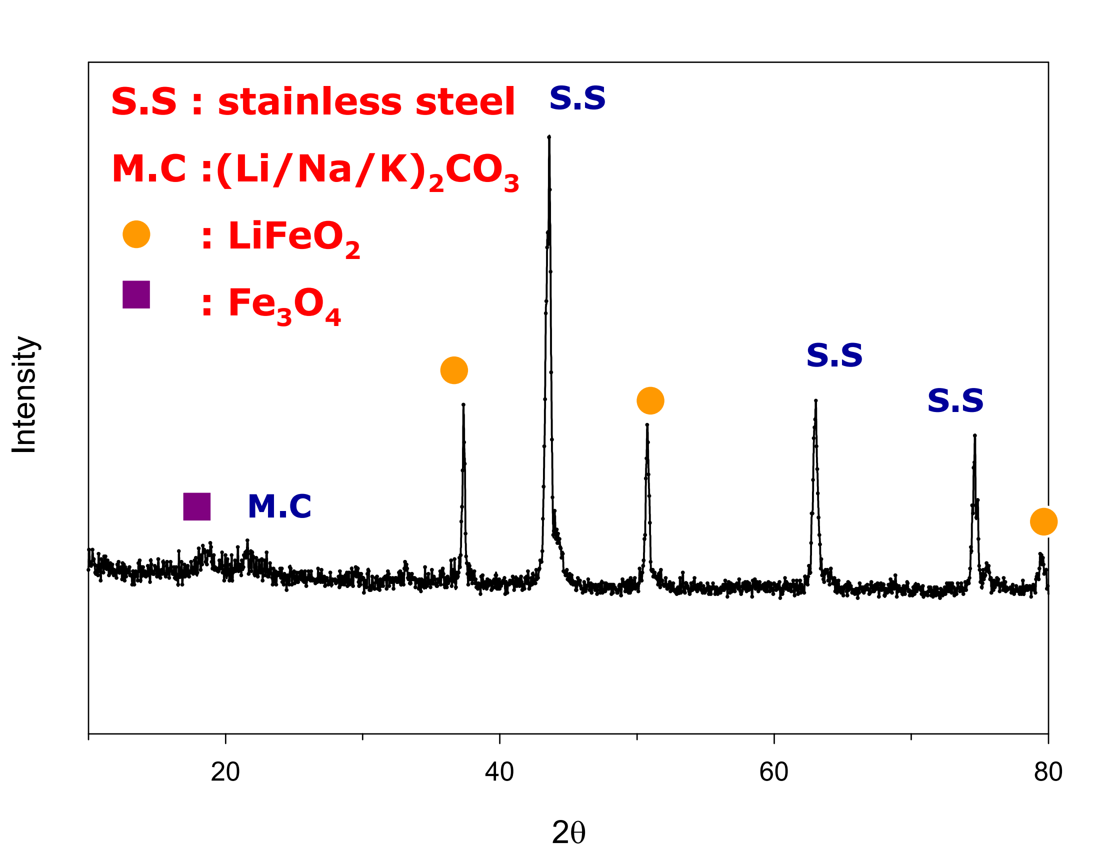
XRD pattern of dual-phase membrane & molten carbonate

XRD analysis after permeation



XRD pattern of membrane after CO_2 permeation at 500ºC

XRD analysis after permeation



XRD pattern of membrane after CO_2 + O_2 permeation at 600ºC

Accomplishments

- **Dense and stable dual-phase metal-carbonate membranes were successfully prepared by direct infiltration method. He gas-tightness of dual-phase membrane was 10^{-6} times higher than that of metal support.**

- **Permeance of CO_2 with O_2 increases with temperature and reaches the optimum at 650°C. Maximum ratio of CO_2/N_2 permeance was about 16 and CO_2 permeance was $7x10^{-8}$ mol/s.m^2.Pa.**

- **At higher temperature, membrane was deactivated due to oxidation, causing a significant decrease in permeance of CO_2 with O_2. XRD results shows that Iron oxide was formed on the membrane after CO_2 with O_2 permeation experiment .**

Future work

- **Ceramic-carbonate system for CO_2 separation**
  - Deactivation of metal carbonate membrane is caused by oxidation of support or reaction of metal support with molten carbonate.
  - Perovskite type ceramic support (Lanthanum Cobaltite) is an alternative support with better oxidation resistance than metal and good electronic conductivity.

- **Multi-component separation experiment**
  - Design and setup new separation/permeation setup
  - Perform separation of CO_2 from mixture of N_2, CO_2, O_2

Alternative support

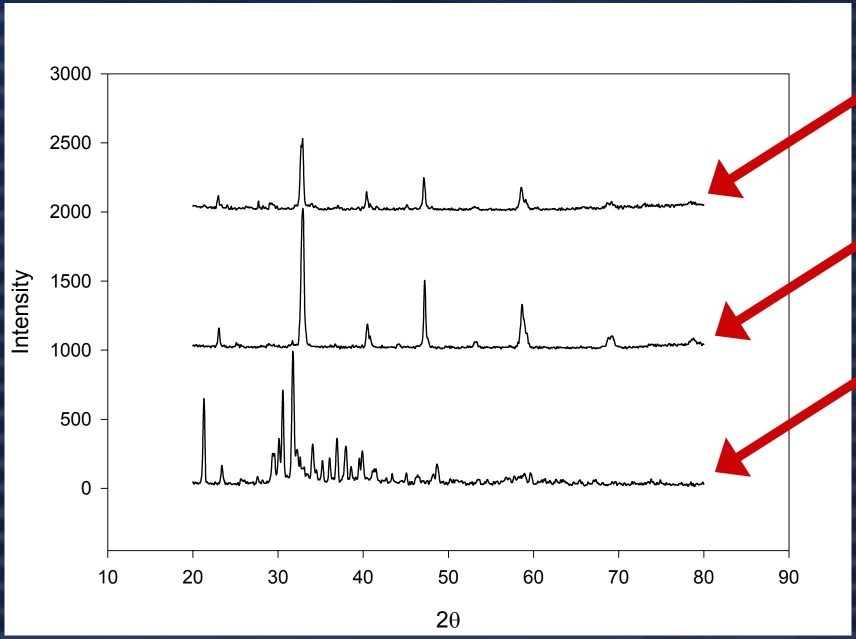
Porous ceramic support

Material	Lanthanum Cobaltite
Composition	$La_aSr_bCo_cFe_dO$ a:b:c:d=6:4:8:2
Electrical Conductivity	1200-1500 S/cm (400-600°C)
Preparation Method	Citrate Method

Preparation of ceramic supports

Step	Details
Precusors	$La(NO_3)_3.6H_2O$, $Sr(NO_3)_2$, $Fe(NO_3)_3$. $6H_2O$, $Co(NO_3)_3.6H_2O$
Polymerization	100-105^{o}C, stirring, 5h
Vaporization	100-105^{o}C, 5h
Powder Drying	110^{o}C
Self Ignition Step	400^{o}C, 1hr
Preliminary Sintering	600^{o}C, 5-24hr
Final Sintering	900^{o}C, 20hr, Ramping Rate 2^o C/min

Reactivity of LSCF + carbonate mixture



LSCF + Li/Na/K carbonate

LSCF perovskite powder

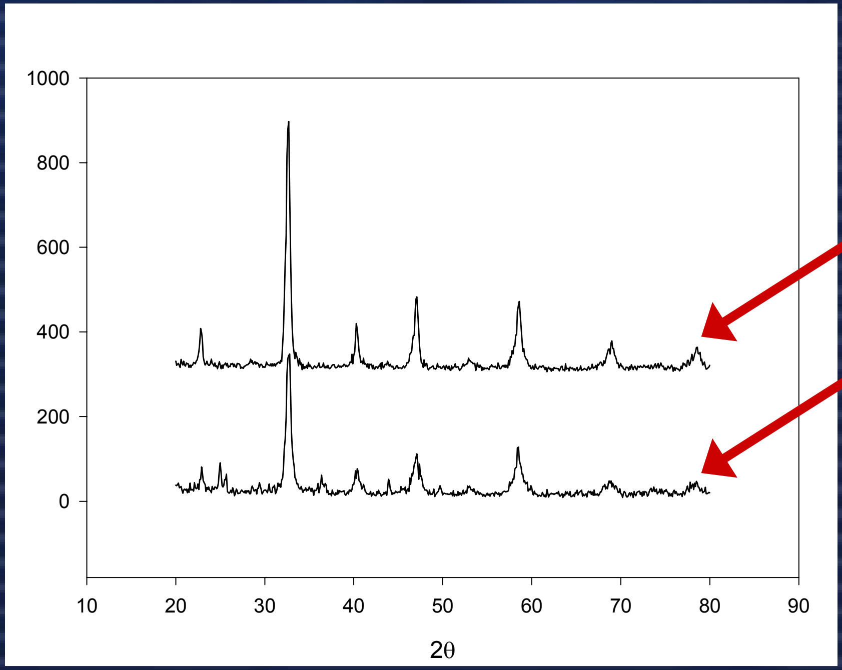
Li/Na/K carbonate powder

XRD peaks of LSCF + Carbonate mixture (600^oC, overnight)

Electronic conduction of the support

Electron-

conductive



After final sintering at 900°C

Before final sintering at 900°C (sintered 600°C)

not

Conductive

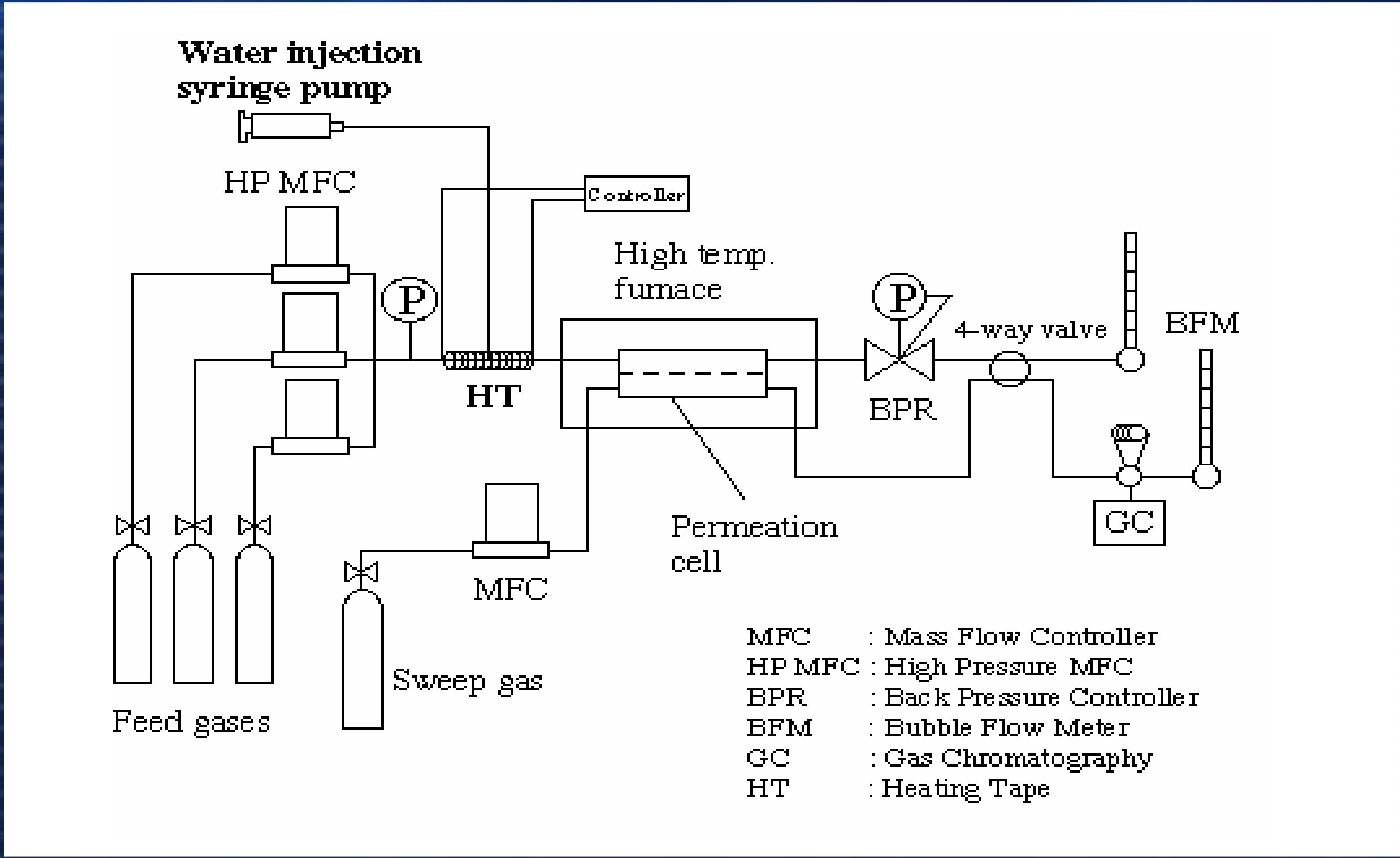
Before & After Final sintering 900°C, 24h

Comparison of support

Support	Porous 316LSS (Grade 0.5)	LSCF support	α-Alumina
Permeance ($mol/s.m^2.Pa$)	1.0×10^{-4}	1.1×10^{-5}	8.0×10^{-6}
Mean pore size (μm)	5.8	2.2	1.0

- Variables to control pore size distribution → Particle size, Sintering temperature

Multicomponent separation system



Thank you for your attention

(cont'd)

Permeance of CO_2, N_2, O_2+CO_2 and their selectivity at 450-700 °C

Temp. (°C)	Permeance (mol/s.m2.Pa) x 10^{-10}			Selectivity	
	CO_2	N_2	$O_2 + CO_2$	CO_2 / N_2	$O_2 + CO_2 / N_2$
450	93.00	116.24	209.24	0.80	1.80
500	116.24	66.44	243.60	1.75	3.67
550	93.00	69.76	321.48	1.33	4.61
600	139.48	46.48	487.16	3.00	10.48
650	162.72	46.48	744.00	3.50	15.98
700	121.28	35.76	432.56	3.39	12.09
750	46.68	39.80	93.36	1.17	2.34